X-ray Powder Diffractometry Using the Empyrean X-ray Diffractometer

1 Scope

1.1 This document provides the procedure for the identification of unknown materials with regularly repeating molecular structure by x-ray powder diffractometry using the Malvern-Panalytical Empyrean by Geologist-Forensic Examiners within the Trace Evidence Unit (TEU) and caseworking personnel who analyze paints and polymers within the Chemistry Unit.

1.2 A crystalline powdered material, a crystalline material on a substrate, or a material with a regularly repeating molecular structure may be used for x-ray diffractometry analysis.

2 Equipment/Materials/Reagents

- Chiller capable of providing chilled water cooled to 70°F at 3.5 to 6 liters per minute flow rate
- High quality drinking water
- Jun-Air Model 6 Compressor or equivalent
- International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF)
- Malvern-Panalytical Empyrean x-ray diffractometer (XRD) or equivalent
- National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 1976, XRD Instrument Sensitivity, Alumina Plate
- Silicon alignment standard
- Additional materials may be used at the discretion of the examiner

3 Standards and Controls

3.1 QA/QC analyses will be performed monthly to verify the alignment of the instrument when instrument is in use, or prior to analysis when instrument has been idle for more than one month.

3.1.1 Analyze the silicon alignment standard using the silicon alignment analysis program (Si Std Spinner Stage).

3.1.1.1 The 100% peak for the silicon alignment standard must be at 28.443 degrees two theta ± 0.05.

3.1.1.2 The third highest peak for the silicon alignment standard must be at 56.123 degrees two theta ± 0.05.

3.1.2 Analyze the NIST 1976 intensity standard using the NIST 1976 intensity analysis program (NIST 1976 Spinner Stage).

3.1.2.1 The peak height of the 100% peak for the NIST 1976 intensity standard should be greater than 4,000 counts.

3.1.2.2 If the intensity falls below 4,000 counts repeatedly, the instrument may need service or a new x-ray tube.

3.2 If the instrument readings for the QA/QC analyses fall outside of the acceptable range, the instrument will be taken out of service until it can be remediated. The instrument is to be aligned by Malvern-Panalytical technical support on an as needed basis when the instrument is not in compliance with the QA/QC check outlined in section 3.1.1.1 and 3.1.1.2. X-ray tube replacement or instrument alignment is to be performed by Malvern-Panalytical technical support on an as needed basis when the instrument is not in compliance with the QA/QC check outlined in section 3.1.2.1.

4 Sampling

At the discretion of the Examiner, the entire sample or components of interest may be analyzed. Individual components or mixtures of components may be removed from the sample for identification as necessary (see Trace Evidence Procedures Manual, *Sample Preparation: X-ray Powder Diffraction* or Chemistry Unit, Paints and Polymers SOP Manual, *X-ray Diffraction Analysis of Tapes*, as appropriate). These individual sub-samples may not be representative of the entire sample. Sub-samples are chosen based on the need to identify a particular component by XRD, and by its availability or presence in a sample.

5 Procedure

5.1 Instrument Start-up

5.1.1 Turn the power on using the wall switch.

5.1.2 Turn the system computer on.

5.1.3 Turn the chiller on.

5.1.4 Turn the compressor on.

5.1.5 Press the “Power On” button to start the XRD. The instrument will go through an initialization procedure which may take up to three minutes. Proceed to the next step once the instrument has finished initializing.

5.1.6 If there is no reading in the kV/mA windows, check to see that the key is set to the on position.

5.1.7 Launch the *Data Collector* software program on the system computer.

5.1.8 Select the Instrument drop-down menu, click on <Connect>, and choose the appropriate stage configuration, and click <OK>.

5.1.9 Adjust voltage (kV) then the current (mA) to the desired analysis conditions. In order to maximize x-ray tube life, the highest recommended setting is 45 kV and 55 mA. Voltage settings should be chosen by the operator based upon the nature of the sample and the requirements of the analysis. 45 kV and 40 mA are appropriate for most geologic materials.

5.1.10 If the instrument had been off, wait at least 2 hours for tube warm-up prior to analyzing samples. If the instrument had been at resting conditions, wait at least 40 minutes for tube warm-up prior to analyzing samples.

5.2 Instrument operation

5.2.1 Prepare sample(s) to be analyzed according to the Trace Evidence Procedures Manual, *Sample Preparation: X-ray Powder Diffraction* or Chemistry Unit, Paints and Polymers SOP Manual, *X-ray Diffraction Analysis of Tapes*, as appropriate.

5.2.2 Insert sample holder in chamber, being careful not to touch sample.

5.2.3 Choose analysis conditions (e.g., scan speed) appropriate for the sample analyzed and the data required. Analysis conditions can be manually entered into the instrument software, an analysis program may be created in the software, or already existing analysis programs can be used when analyzing samples.

5.2.4 If phase identification is desired, compare the resulting scans to scans published in the ICDD PDF.

5.3 Instrument shutdown

5.3.1 When the analysis session is complete, remove the samples from the chamber, and return the instrument to normal resting conditions: chiller on, compressor on, XRD on, voltage set a 30 kV and current set at 10 mA. Exit Data Collector.

5.3.2 If it is necessary to shut the system off, use one of the following methods:

5.3.2.1 Routine shutdown

5.3.2.1.1 From *Data Collector*, select the Instrument drop-down menu and click on <Disconnect>.

5.3.2.1.2 Push the "Off" button on the instrument.

5.3.2.1.3 Switch off the main power switch on the back of the instrument.

5.3.2.1.4 One to two minutes after the system has been powered off, turn off the chiller.

5.3.2.2 Emergency shutdown

5.3.2.2.1 If there is a need to immediately shut down the instrument, press the red "Emergency Off" button on the front of the instrument. NOTE: pressing this button will immediately cut off the main power supply, but the control panel and safety circuits will stay live.

5.3.2.2.2 If possible, wait one to two minutes and turn off the chiller.

5.3.2.2.3 In the event that the "Emergency Off" button is depressed, the button must be unlocked before the instrument can be switched on again. To unlock the button, turn the button clockwise until the button moves out.

5.3.2.3 Emergency power off

5.3.2.3.1 If there is a need to immediately shut off power to the instrument, pull down on the emergency cut-off switch on the wall behind the instrument.

5.3.2.3.2 If it is possible to wait, wait one to two minutes and turn off the chiller.

5.4 Instrument Maintenance

5.4.1 The instrument is serviced twice yearly by Malvern-Panalytical, Inc. technicians.

5.4.2 The water level in the chiller reservoir must be between the float and the threaded fill neck. If the water level is low, add high-quality drinking water to the reservoir.

6 Calculations

Not applicable.

7 Measurement Uncertainty

Not applicable.

8 Limitations

8.1 Only materials with regularly repeating molecular structure may be identified by XRD.

8.2 Peaks may be difficult to resolve in mixtures with large numbers of components.

8.3 Small samples, components in small quantities in a mixture, and low symmetry or poorly crystalline minerals in a mixture may diffract insufficient x-rays for detection.

8.4 Preferred orientation can result in suppression or enhanced expression of peaks.

9 Safety

9.1 The x-ray diffractometer generates x-rays while in operation. Exposure to x-rays is a health hazard. All operators must wear an x-ray radiation monitoring badge during operation of the instrument.

9.2 The instrument is shielded from leakage and is outfitted with various interlocks to prevent the accidental leakage of x-rays. Never override the safety interlocks. The shutter must be in the closed position prior to removing a sample.

9.3 The instrument requires high electrical voltage. Use extreme caution to avoid electrical shock when accessing those portions of the instrument carrying current. The voltage on the HT cable decays slowly to zero when the generator is turned off and may therefore be a shock hazard even when the generator is off.

9.4 The x-ray tube and detector contain beryllium windows. Beryllium is poisonous. Avoid contact with the beryllium windows. Using soap and water, immediately wash any body parts that accidentally come in contact with beryllium windows.

9.5 Universal precautions will be used and at least the minimum appropriate personal protective equipment (PPE) will be worn when handling samples, the x-ray tube, or detector.

10 References

- Buhrke, Victor E., Ron Jenkins, and Deane K. Smith, *A Practical Guide for the Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis* (New York: Wiley-Vch, 1998).

- Cullity, B. D., *Elements of X-Ray Diffraction* (Reading, Massachusetts: Addison-Wesley Publishing Company, Inc., 1978).

- Jenkins, Ron, and Robert L. Snyder, *Introduction to X-Ray Powder Diffractometry* (New York, New York: John Wiley & Sons, Inc., 1996).

- Moore, Duane M., and Robert C. Reynolds, Jr., *X-ray Diffraction and the Identification and Analysis of Clay Minerals, second edition* (New York: Oxford University Press, 1997).

- Pecharsky, Vitalij K., and Peter Y. Zavalij, *Fundamentals of Powder Diffraction and Structural Characterization of Materials, second edition*, (New York, New York: Springer Science+Business Media, LLC, 2009).

- Skoog, Douglas A., F. James Holler, and Timothy A. Nieman, *Principles of Instrumental Analysis, fifth edition* (Philadelphia, Pennsylvania: Harcourt Brace College Publishers. 1998).

- Sample Preparation: X-ray Powder Diffraction, Trace Evidence Procedures Manual (current version).

Rev. #	Issue Date	History
0	06/15/2020	New document.
1	09/01/2021	Added Section 3.1.2.2. Changed “Mineralogy” to “Geology” in Approval Section. Updated TL in Approval Section.

Approval

Redacted - Signatures on File

Trace Evidence Unit Chief _____ Date: 08/31/2021

Geology Technical Leader _____ Date: 08/31/2021

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Paints and Polymers Technical Leader _____ Date: 08/31/2021